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THE ELECTRODEPOSITION OF ANTI-
MONY.

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THE ELECTRODEPOSITION OF ANTIMONY

by

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A Thesis Submitted for the Degree of

BACHELOR OF SCIENCE

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The electrodeposition of antimony from chloride solutions seem to have attracted the attention of chemists, probably because of the fine appearing deposit. For a long time the exact character of the deposit was not known until Gore found that the antimony thrown down from the chloride solution was explosive when heated to a low temperature or struck with some hard substance. The amount of heat generated by said explosion was measured under different conditions.

In continuation of this line of work, deposits were obtained by the writer starting with a chloride solution of the following composition

	: Rate of 40gr. SbCl_3
50 cc SbCl_3 solution :	
	: to 25 cc HCl

75 cc H_2O

HCl enough to dissolve precipitate.

and varying the amounts of acid in solution. With each change of acid concentration the effect of different current densities and temperatures were noted, with the conclusion that the essential characteristic of the deposit, its explosive nature, remained practically unchanged. In an analysis by G. Gore a deposit of antimony

from a chloride solution was shown to have the following composition.

Antimony	93.36	93.51
SbCl_3	5.98	6.03
HCl	.48	.21

In the work of the writer the exact composition was found to vary. This conclusion was arrived at because the temperature necessary to start the reduction was not always the same. Samples tried showed that deposits obtained when the solution was at a temperature of from 20 to 25 ° Centigrade exploded easily and with a general explosion while samples from solutions at 50° or 90° Centigrade exploded only in the spot heated. The only reason for this seemed to be that deposits from a warm or hot solution contained less of the impurities which made the antimony explosive.

The appearance of the deposit from a cold or 20-25° Centigrade solution was bright and lustrous of a silvery white color. As the temperature of the solution increased the deposit became more gray, losing its bright lustrous appearance until from a 90° solution the polish had apparently disappeared leaving a smooth explosive deposit of a color almost as gray as the pure

crystal.

The addition of gelatine in small quantities, from .5 to 1. gram per 150 cc solution did not materially affect the explosive character of the deposit. With an increase of gelatine in the electrolyte the deposit gradually lost its grayish color until with an excess it assumed a burnished black appearance.

The variation of current density between .07 to .2 amp. per sq. in. had little effect upon the deposit.

The increase of acid in the solution made the explosion take place at a lower initial temperature.

The deposits obtained at room temperature from the pure chloride solution, as examined under the microscope, for current densities varying from .06 to .2 amp. per sq. in., were smooth and not crystalline or nodular. As the temperature of the electrolyte increased the deposits passed through a stage of dull gray roughness to a deposit at 90° which was rougher and which had a tendency to crystalline structure. Although the appearance of the deposit was changed slightly by the addition of gelatine, as stated before, the structure of the deposit was almost exactly the same as with the pure chloride solution, that is, it became rougher when precipitated

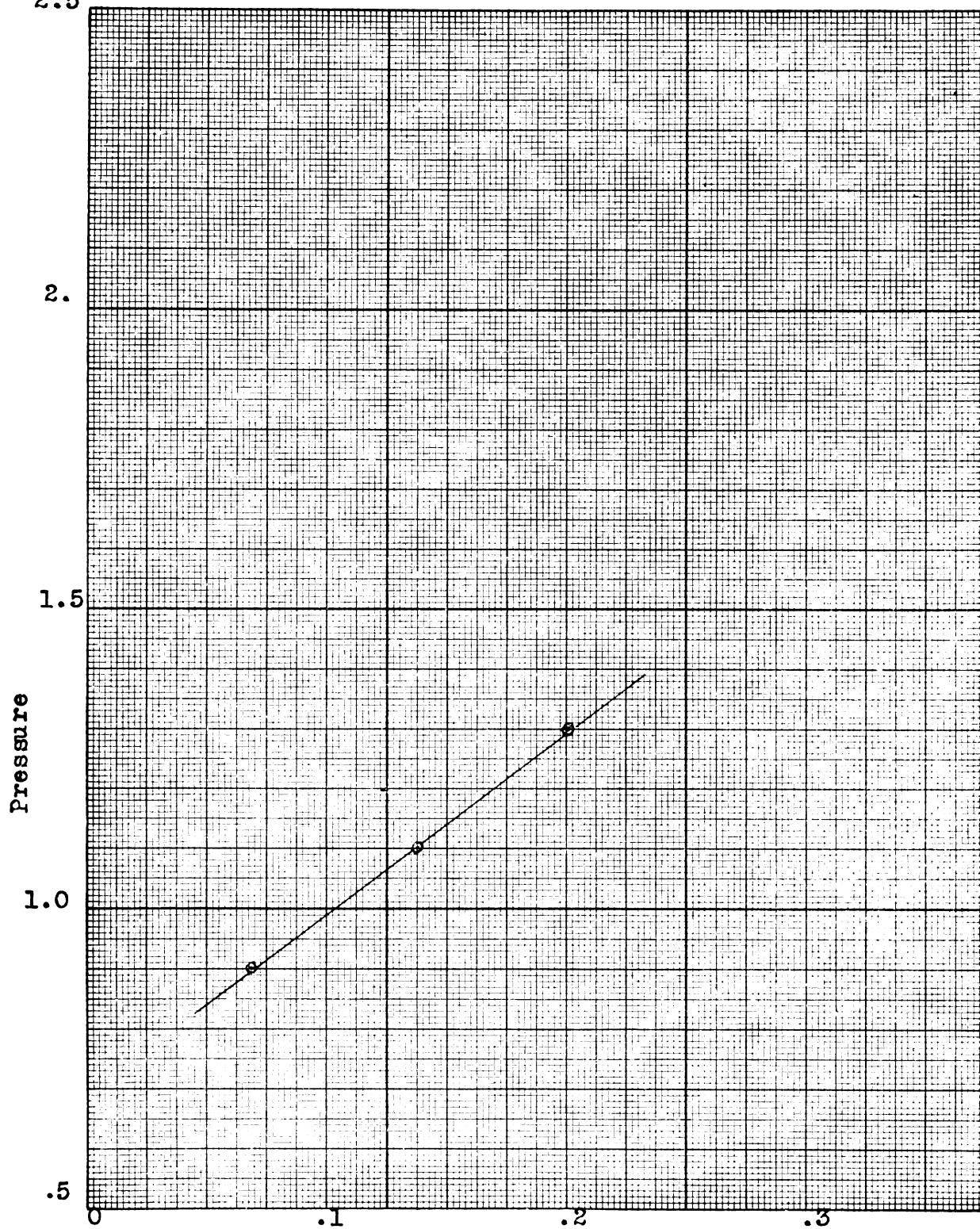
hot solutions and the current density had little effect upon its appearance.

The following tabulated data and curves give a better idea of the exact effect of current density and temperature changes.

Comparison Effect of Current Density in Chloride Solution.

Composition of Solution	Amp. per sq. in.	Volts	Temp.	Color Deposit	Character of Deposit
50 cc Cl sol. 75 cc H ₂ O HCl to dissolve precipitate	.068	.9	23°	Silver gray	burnished ex- plosive not crystal or nodular.
" "	.137	1.1	23	"	" "
" "	.204	1.3	23	"	" "

2.5 Current Density Pressure Curves for Chloride Solution.



Current Density. Amp. per sq.in.

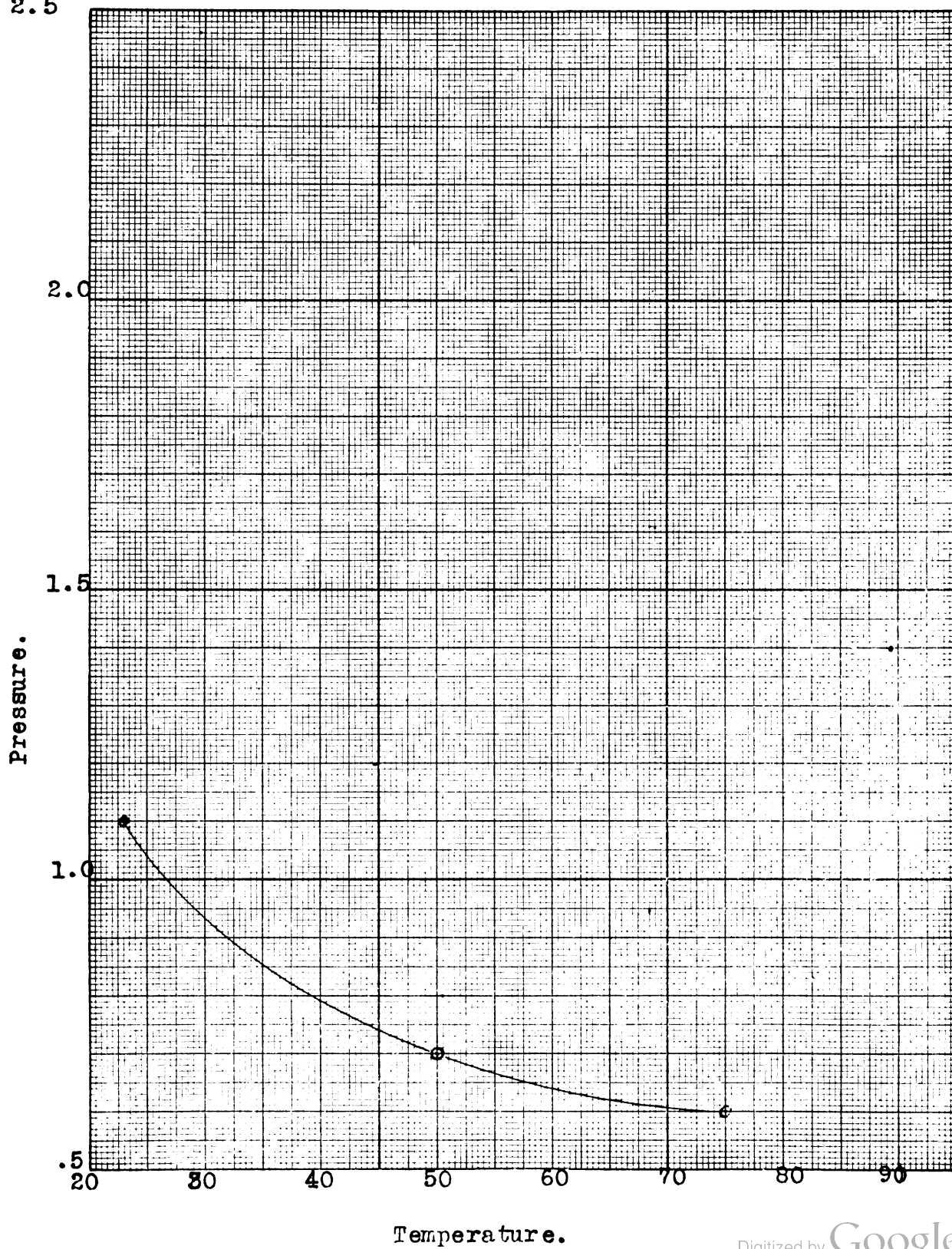
Effect of Temperature on Deposit.

Composition of Solution	Amp. per sq. in.	Volts	Temp.	Color of Deposit	Character of Deposit.
50 cc. Cl.sol. 75 H ₂ O HCl to dis- solve precip.	.137	1.1	23°	silver gray	smooth, burnish- ed explosive, low initial explosion temperature.
" "	.137	.7	50°	steel gray	rougher, unburn- ished explosive medium explosion temperature.
" "	.137	.6	75°	steel gray	rough, tends to crystalline. un- burnished explo. high initial explo. temp.

Tartaric acid was added in small amounts to a chloride solution of the above composition principally to see what effect it would have upon the explosiveness of the deposit. The addition of tartaric acid in small quantities 1-5 cc. concentrated solution reduced the reflective power of the deposit yet left the deposit smooth, gray and bright, as if a crystalline deposit were polished mechanically. The effect of the acid did not become pronounced until almost one tenth of the solution was acid. The deposit with an excess of acid

Temperature Pressure Curve for Chloride Solution. 7.

2.5



was darker, having lost the grayish appearance and assumed a bluish gray. With the increase of temperature the brightness disappeared and the deposit became dull white. The burnishing of such a deposit gave a steel white color. The explosive character was decreased with the addition of the acid until with an excess, .1 acid, the explosion was not general and a high temperature was necessary to produce even a crackling sound. The explosion caused the deposit to curl up and drop from the electrode in small corrugated particles. This, however, was not true when the deposit was taken from a hot or from a strong acid solution. In such cases the metal had a tendency to curl, but generally remained flat on the plate on which it was deposited until the plate was bent. This relieved the strain and as the particles fell off they curled to a slight extent.

The following tables give the observed effect of temperature and acid concentration upon the deposit. The current density table is omitted because, as in the previous case, the moderate range .06 to .1 amp. per sq. in. had little effect compared with the other influences.

A microscopic study of the deposits showed that acid in small quantities at room temperature gave a smooth deposit, while acid in excess produced a rough nodular precipitate. The effect of temperature was the same as with the pure chloride solution, and with a temperature of only 50° Centigrade a rough gray, even nodular effect was produced. These facts are given more in detail in the following tabulated data.

Temperature Effect in Tartaric Chloride Solution.

Composition of solution.	Ampere per sq.in.	Volts	Temp.	Time of explosion heating at constant temperature	Character of Deposit.
50 cc Cl solution H ₂ O to neutral- ize acid 5 cc. conc. tartaric acid.	.109	1.2	23°	20 sec. general explosion	Flies from plate
" " "	.109	.8	50°	20 sec. little crackling	Adheres to plate.

Acid Concentration Effect Tartaric Acid.

Composition of Solution	Amount of Acid	Current Density	Volts.	Temp. C.	Time of Explosion.
50 cc Cl sol. H ₂ O to neut- ralize acid	1 cc. con- centrated solution of tartaric acid	.109	.5	23°	10 seconds general explosion.
" "	5 cc. sol- ution	.109	1.2	23°	20 seconds general explosion.

It will be easily seen from the discussion just given that the explosive nature and the appearance of the deposit are closely related. With the increase of temperature, tartaric acid or gelatine in solution the burnished appearance was replaced by a gray, rougher, less explosive deposit. The beauty of the burnished deposit must be sacrificed if a precipitate is to be obtained which is non-explosive.

As it seemed impossible to obtain a good bright deposit from a chloride solution without its being explosive, a fluoride bath was substituted, with fair success.

A solution of the composition

75 gr. antimony fluoride
100 cc. hydrofluoric acid
470 cc. water.

was used and the effects of the variation of temperature, current density, richness in antimony fluoride, and acid concentration were studied.

All of the runs from the fluoride solution were of one hour duration.

The current density was varied from .068 amp. per sq. in. to .39 amp. per sq. in., when the solution was at a temperature of 20 to 23° Centigrade.

The size of the crystals does not change with the variation of current density if the ampere hours is kept constant, but the compactness of the deposit and the current density seem to vary proportionally. With the density of .07 amp. per sq. in. crystals were formed on the surface of the cathode in a scattered manner such that hardly two crystals were in contact. Instead of spreading over the surface of the cathode, crystals grew upon crystals forming nodules composed of crystals at all angles. As the current density increased the surface of the cathode was more evenly covered. With a current density of .39 amp. per sq. in. the nodules

were fairly compact thus losing the nodular appearance and giving a rough jagged crystalline surface. The voltage had a tendency to drop in the course of an hour generally about .05 of a volt.

The deposit in all cases was silver gray and the crystals were very refractory.

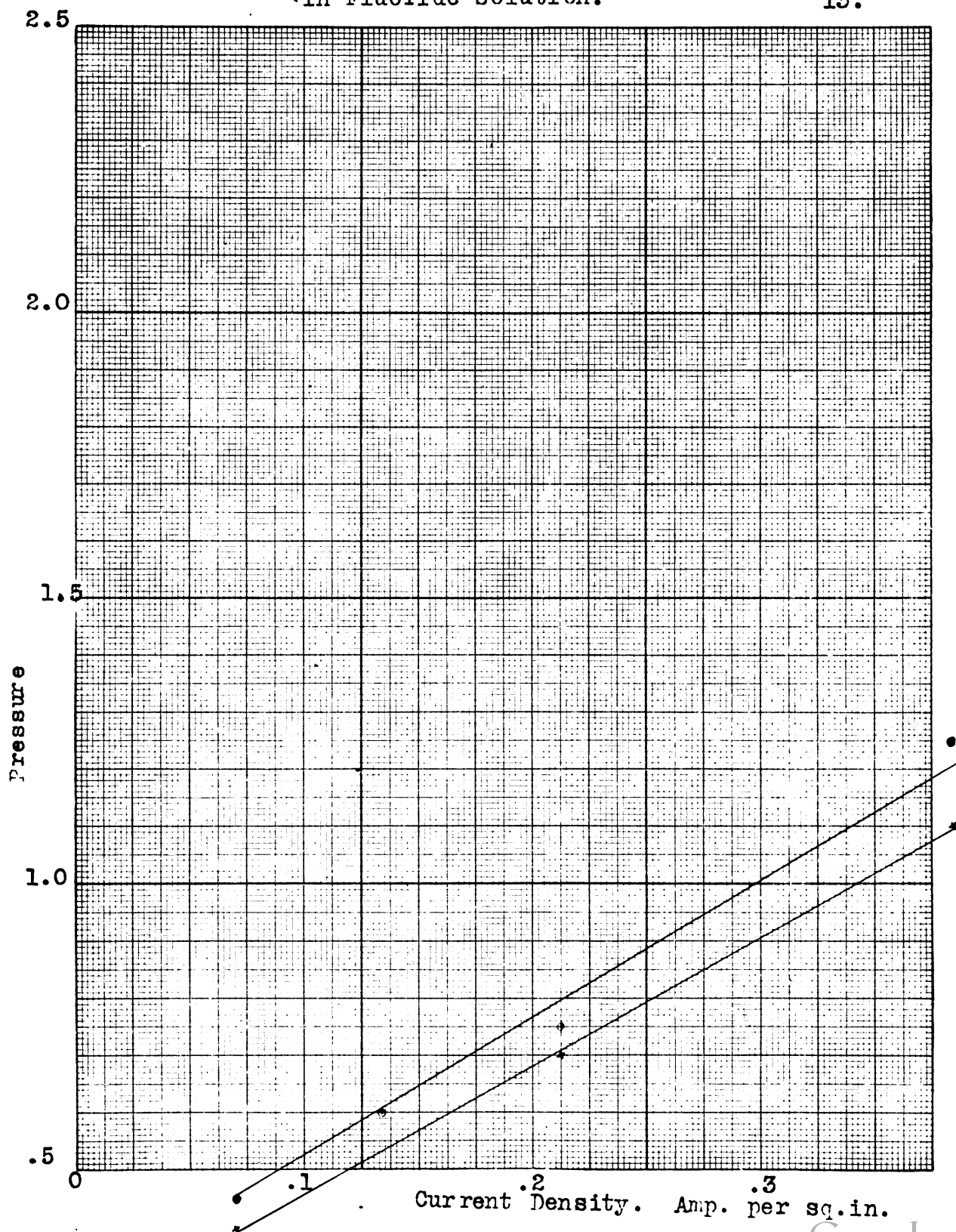
The effects of changes of current density and temperature are given below in tabulated form, also the same results plotted.

Pure Fluoride Solution.

Solution	Temp.	Current Density	Volts before	Volts after	Deposits under Microscope.
75 gr. SbF_3 100 cc HF 470 cc H_2O	22	.068	.45	.4	#1 Nodular, crystalline, scattered sparingly over surface.
" "	22	.133	.6	--	#2 Larger crystals, more compact than #1, jagged crystalline surface.
" "	22	.215	.75	.7	#3 Larger crystals more compact than #2, flat crystals piled in hit or miss style.
" "	22	.386	1.25	1.1	More compact than #3, crystals also larger

Variation of Current Density and Voltage
in Fluoride Solution.

13.

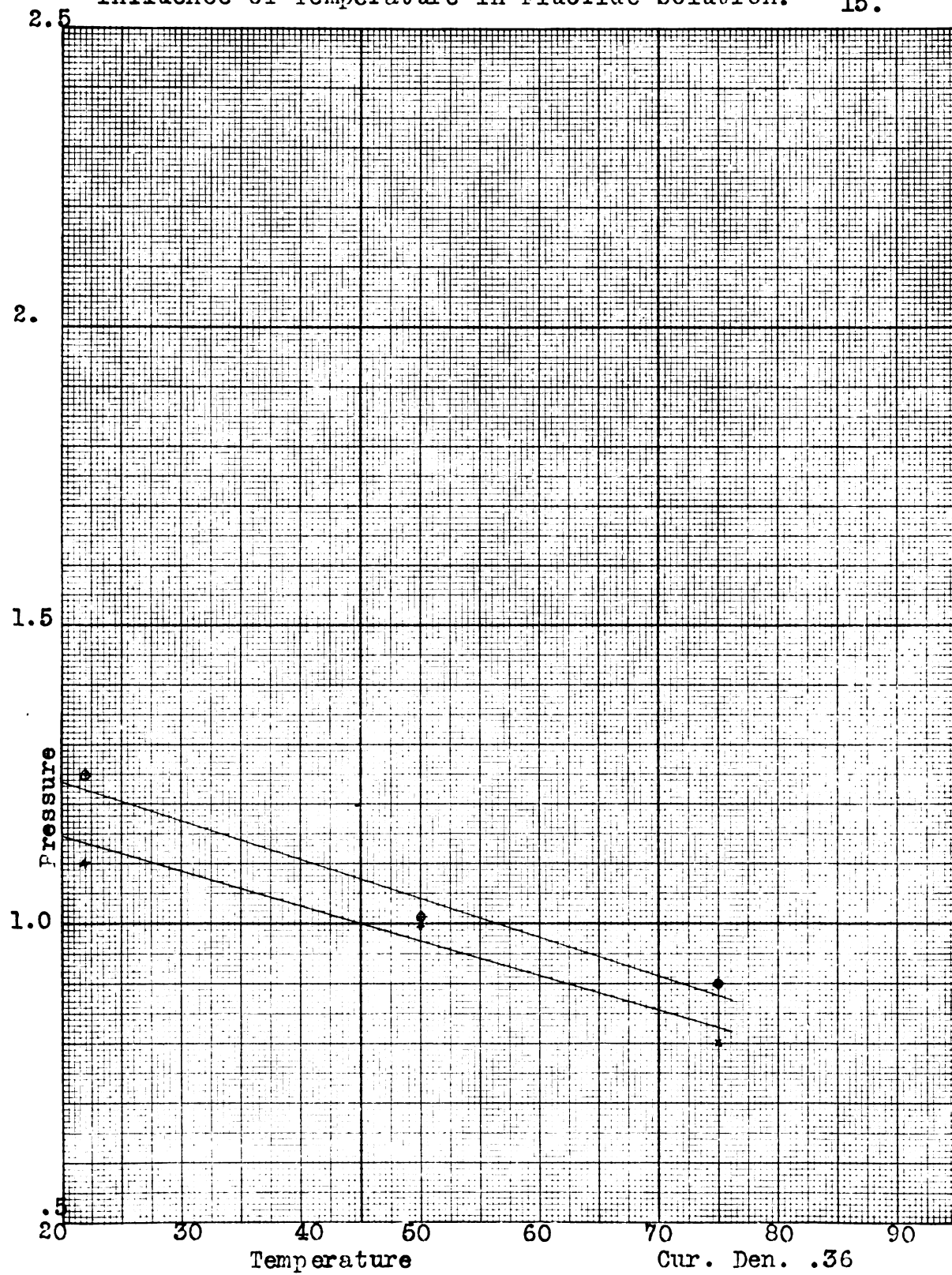


The Influence of Temperature on Pure Fluoride Solution.

Solution	Temp.	Current D	Volts before	Volts after	Deposits under Microscope.
75 gr. SbF_3 100 cc HF 470 cc H_2O .	22	.386	1.25	1.1	#1. Compact nodules of crystals, crystals large.
" "	50	.4	1.01	1.	#2. Smaller crystals and more compact than #1, occasionally some large crystals in with small.
" "	75	.34	.9	.8	#3. Very similar to #2.

With the addition of about .5 of a gram of gelatine, the deposits assumed a darker grayish color. The crystalline flakes were not large and instead of collecting in nodules the gelatine caused the deposit to precipitate in ridges running from the top to the bottom of the cathode, leaving plain copper between the ridges. The crystals were smaller than from the pure fluoride solution. With the addition of gelatine the plain copper surface between the ridges began to fill in with small crystals until with one gram of gelatine the whole surface was covered. The ridges existed yet

Influence of Temperature in Fluoride Solution. 15.



they were made up of very imperfect crystals. With a still further addition of gelatine the deposit became darker and darker, the valleys gradually filled until with 2.5 grams of gelatine the surface was only slightly rolling or wavy. After two grams were added the deposits obtained at room temperature would curl up and peel off if allowed to accumulate for more than a few minutes. The increase of temperature lessened the effect of the gelatine, changed a deposit from a dark, lumpy round cornered deposit to a gray, nodular angular precipitate which tended toward crystallization. With the current density constant, a rise of temperature resulted in an evolution of gas in small quantities, which caused pits to form in the antimony.

The results showing the effect of gelatine are given below in detail.

The Influence of Gelatine in Solution.

Solution	gr. of gelatine	Temp.	Cur.	Volts Den. before	Volts after	Deposit under Microscope.
75 gr. SbF_3	0	22	.205	.75	.7	#1. Crystalline nodular deposit nodules not com- pact after show- ing copper plate between nodules.
" "	.5	22	.205	.75	--	#2. Crystalline flakes not large in ridges piled up. Cu shows be- tween ridges.

With a current density of .34 ampere per sq. in., gelatine was varied from 3.5 grams up to 20 grams with some very interesting results. With the increase of gelatine up to 10 grams the voltage raised proportionally but when the gelatine was increased beyond this point the voltage dropped until with 20 grams it was almost the same as when 4 grams were in the solution. The character of the deposit varied in a peculiar way. As already stated, the addition of gelatine tended to reduce the roughness of the deposit. This tendency was very marked until five grams of gelatine are added. Above this point the tendency was less marked and even

when 20 grams are in the solution the nodules still exist although much smaller.

As noted before, gelatine in small quantities produced a darker and highly burnished deposit. With the fluoride solution this was true up to a point where 7 grams of gelatine were in the solution, at which point the cathode became slightly streaked with a gray deposit. As the gelatine increased beyond this point the gray became more pronounced, the deposit a trifle rougher, until with 20 grams in the solution and with a current density of .34 amp. per sq. in. the deposit was all gray, highly burnished with a few small nodules on the surface, not visible with the naked eye.

The increase of temperature in a solution containing gelatine seemed to have very little noticeable effect upon the structure of the deposit, but the appearance changed from a bright lustrous one, with 2.5 gr. gealtine at 22° Centigrade, to a dull lustrous deposit at 50°. The deposit remained practically unchanged with the change of current density when the ampere hours remained constant. This held for moderate ranges of current density, .075 - .27 ampere per one square inch.

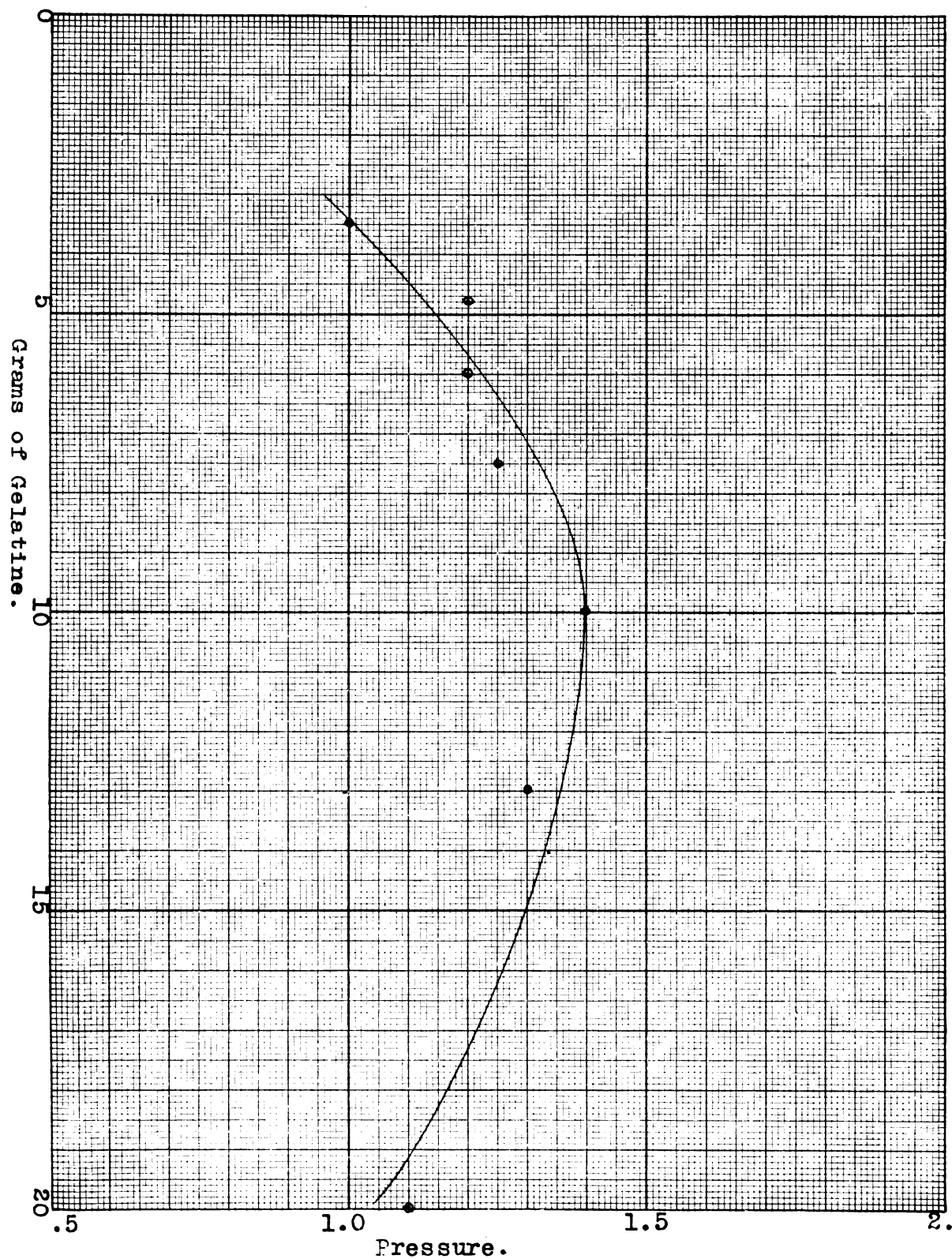
With an increase in the ampere hours the crystals became larger, nodules more prominent and the general character of the deposit rougher.

The changes produced in the electrolyte by the addition of gelatine at different temperatures and different current densities, are tabulated below; also curves showing the same.

The Influence of Gelatine in Fluoride Solutions
at Different Temperatures.

Solution	Temp.	Gram	Volts	Volts	Cur.	Deposit under
		Gel.	before	after	Den.	Microscope.
75 gr SbF_3 100 cc HF_3 470 cc. H_2O	50°	.5	.75	.7	.205	#1. Crystals in sharp ridges, valleys started to fill in with small crystal.
" "	50°	1.	.7	.7	.205	#2. Crystals seem to be imperfect, edges rounding, plate covered yet in ridges.
" "	50°	1.5	.7	.7	.205	#3. Deposits darker the more the gelatine, a little uneven, occasionally a crystal.
" "	50°	3.5	1.		.34	#4. Very rough, dull gray, very highly polished nodules.

75 gr SbF ₃ etc.	50°	4.8	1.2	-- .34	#5. Dark smooth surface, slightly nodular.
"	"	50°	6.	1.2	-- .34 #6. Dark, highly polished, seldom any nodules.
"	"	50°	7.5	1.25	-- .34 #7. Slightly nodular (round cones) highly polished, broken by streaks of gray apparently crystalline deposits.
"	"	50°	10.	1.4	-- .34 #8. General roughness, dark more nodular than #7.
"	"	50°	13.	1.3	-- .34 #9. More gray than #7 with still streaks of dark, smooth deposit.
"	"	50°	20.	1.1	-- .34 #10. More gray, no dark streaks, few small nodules.



Influence of Change of Temperature on Gelatine Solutions.

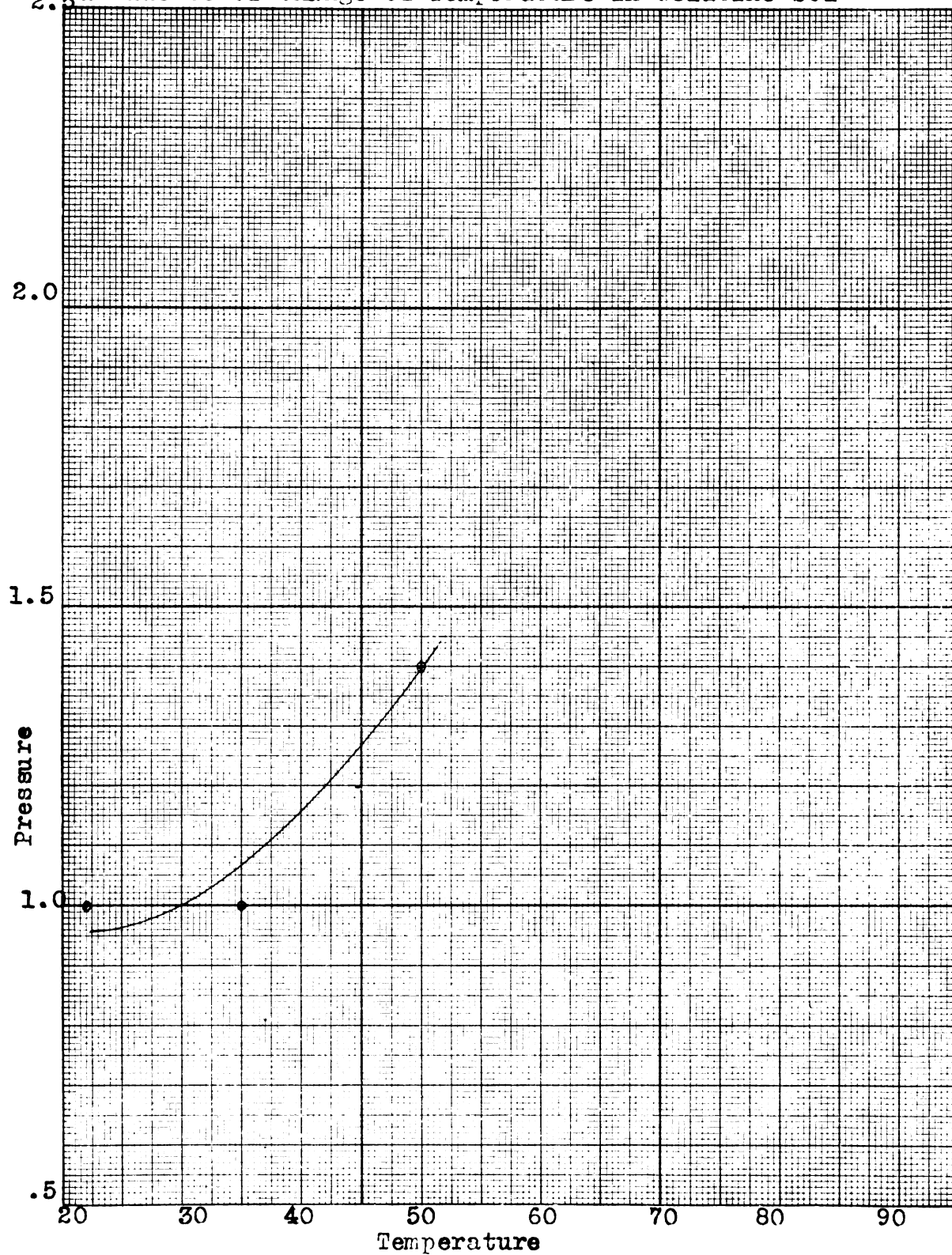
Solution	Temp.	Gel.	Cur.	Den.	Volts	Deposit under Microscope.
75 gr. SbF_3	22°	2.5	.205		1	Lustrous, trifle uneven, not nodular. #
" "	35°	2.5	.205		1	Lustrous, not nodular. #
" "	50°	2.5	.205		1.4	Dull luster, not nodular. #

# Appear to be very finely crystalline.						

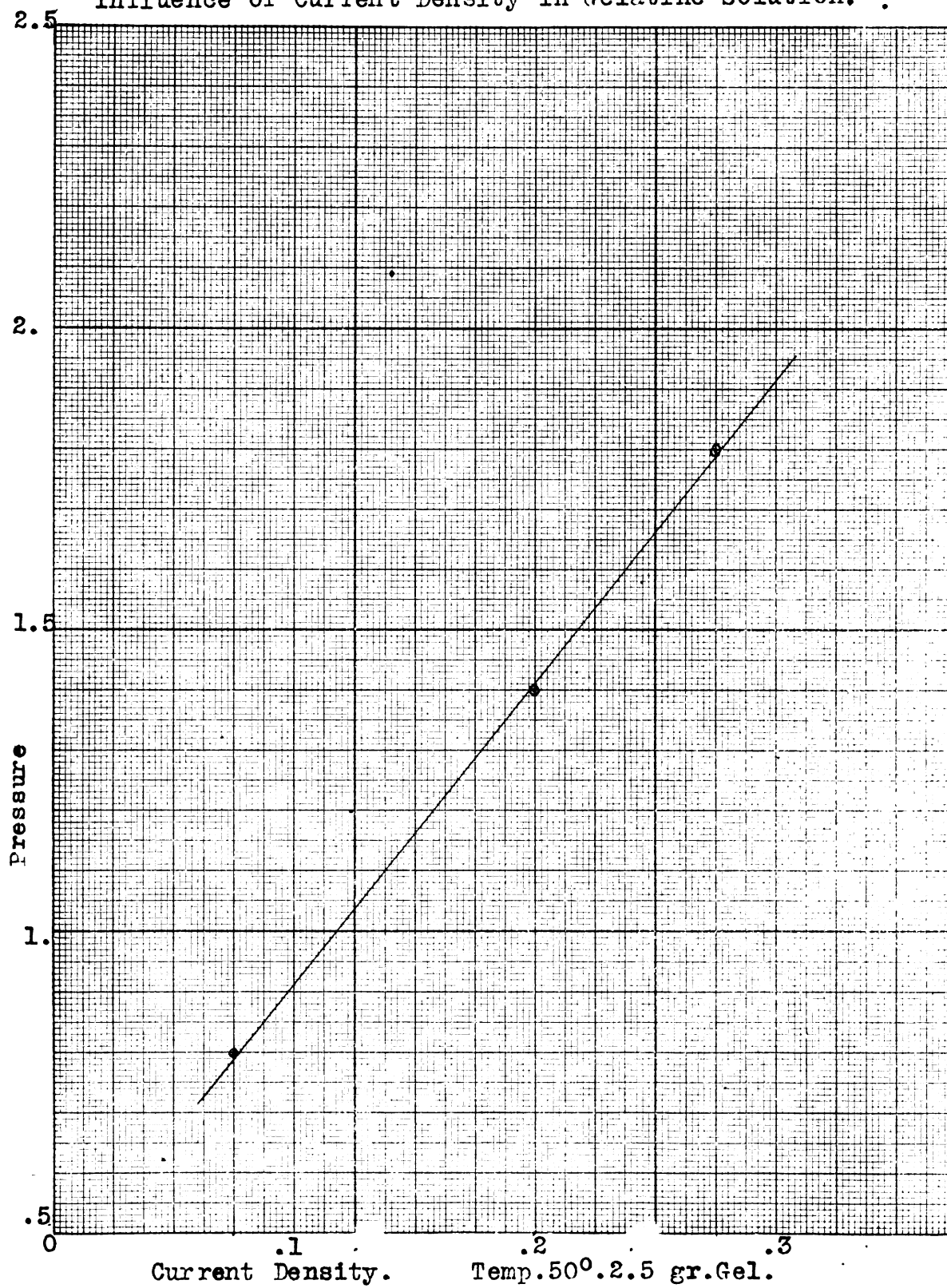
Influence of Different Current Densities in Gelatine Solution.

Solution	Temp.	Gel.	Cur.	Den.	Volts	Deposit under Microscope.
75 gr. SbF_3	50°	.075	.8		2.5	#1 Finely crystalline, fairly smooth, occasionally small nodules on surface.
" "	50°	.205	1.4		2.5	Finely crystalline, smooth, very few nodules.
" "	50°	.272	1.8		2.5	Less smooth, crystals larger than #1, nodules more prominent.

2.5 Influence of Change of Temperature in Gelatine Solution.



Influence of Current Density in Gelatine Solution.



Current Density.

Temp. 50°. 2.5 gr. Gel.

Another solution was tried having a composition the same as that used before except that in place of 100 cc HF, only 50 cc were used. The general discussion of the last case would apply here also. A detailed comparison may be obtained better from a study of the curves. Using a low current density it was found that the deposit covered the surface more completely than in the solution used previously, and the crystals were smaller.

With the above electrolyte the effect of temperature was very great. With a current density of .078 amp. per sq. in., the deposit at 22° although smooth to the touch was crystalline, nodular in ridges and not covering the entire plate, while with the same current density at 50° the deposit was more compact, nodular structure being almost entirely gone, leaving a general crystalline deposit. With a current density of .137 the effect was a little different. The deposit at 22° was quite compact, nodular, smooth to the touch, and copper was plainly visible between the nodules. At 75° the deposit became still darker, compact and evenly crystalline with pits being formed.

The comparison given above brings up the question

of what effect the current density has on the deposit. At the temperature of 22° all of the deposits were crystalline, smooth to the touch, and did not cover the entire plate. The higher the current density, the more compact was the deposit and the less the Cu was visible between the nodules of Sb.

With a low current density as .078 ampere, the deposit seemed to form in ridges, which characteristic was not noticeable with higher current densities. At 50° a low current density gave a dull gray, compact, very even crystalline deposit. This character of deposit was maintained for different current densities until a current density of .335 was used, which gave a gray deposit. The increase in ampere hours did not change the general character of the deposit, but there was a tendency for large crystals to grow out of the surface.

In comparing the effect of change in acid concentration, HF acid was added to a solution of 75 gr. SbF_3 plus 470 cc. H_2O in quantities of 25, 50 and 100 cc. With 100 cc. of acid in the solution, large crystals were formed at a current density of .34 ampere per square inch. The surface was not entirely covered and

felt rough to the touch. With the decrease of acid, the crystals became smaller and with this the increased smoothness and compactness of the deposit.

When gelatine was in the solution, the effect of the acid seemed to give the deposit a more burnished color as in the case of the chloride solution. At a temperature of 50° Centigrade, the solution containing 100 cc. HF and 6 gr. gelatine gave a dark, highly polished surface with scarcely a nodule. With the decrease to 50 cc. of acid, the deposit was slightly nodular, smooth and burnished, and with 25 cc. of acid the deposit showed many very small nodules and pits formed on the surface, causing the deposit to lose some of its burnished effect.

With the change of amount of SbF_3 in solution, the deposit changed but slightly, the crystals became larger as the amount of antimony fluoride was reduced.

In trying alloys of lead and antimony from a fluoride solution, the solution of antimony fluoride was kept saturated with lead fluoride by constantly having a solution containing lead oxide stirred. With a low current density of .06 ampere per square inch, an alloy was obtained containing 80 per cent Sb. This deposit

was bright, smooth with small cones. As the current density was increased, the percentage of antimony fell off until from a solution at 50° Centigrade and a current density of .34 ampere per square inch, the percentage dropped to 38.55.

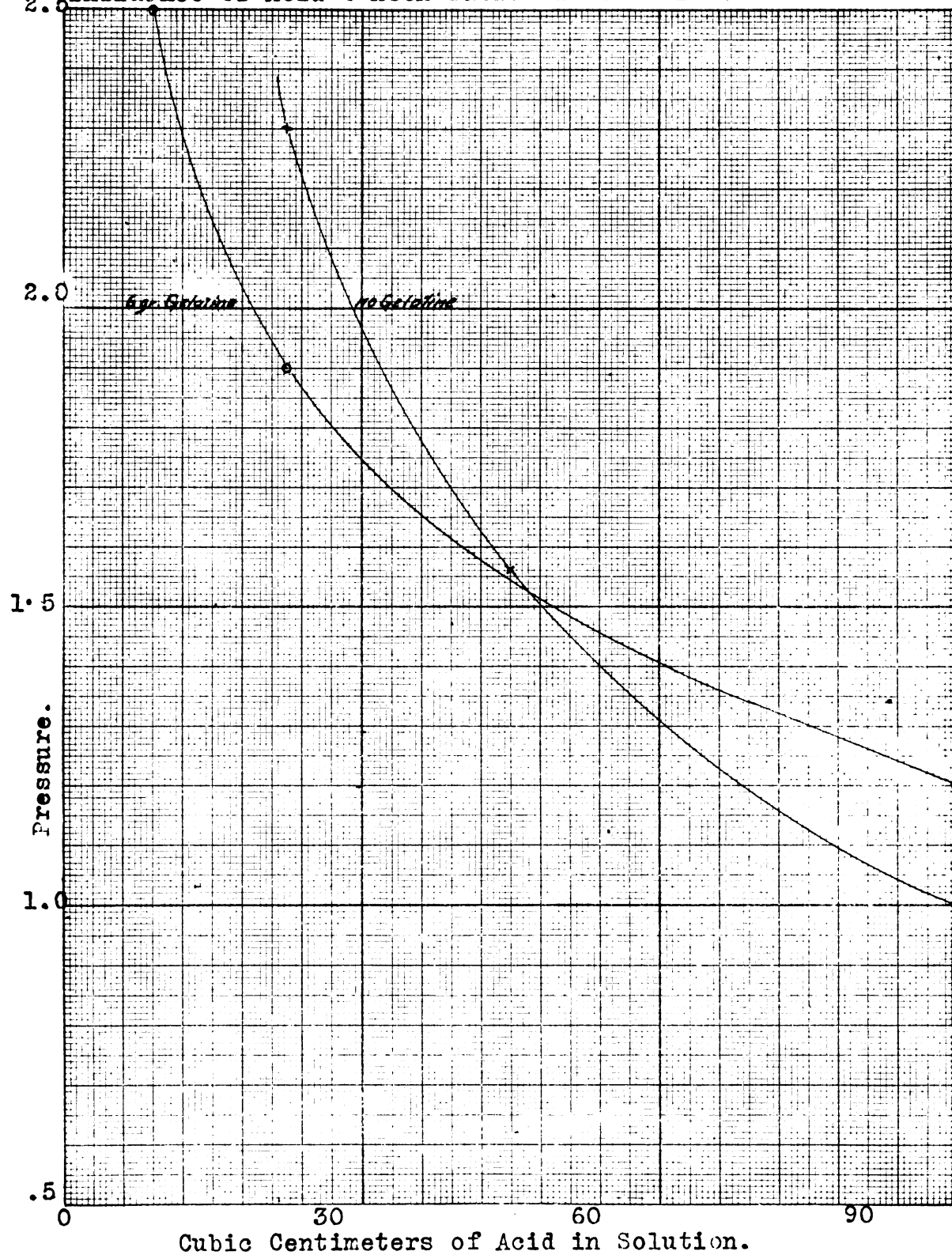
The deposits, in all these cases, were brittle, showing that although a good alloy could be obtained of lead and antimony, it was almost impossible to get an alloy that would stand bending and still contain enough antimony to make it bright and lustrous. Gelatine in the double fluoride solution did not help to any great extent. When the current density had reached .1 ampere per square inch, the surface began to lose its bright lustrous appearance, became gray and nodular. At .27 ampere the deposit had a tendency to tree at the edges of the electrode similar to lead, and had much the same appearance yet considerably grayer. With a current density of .34 ampere the nodules were very prominent and large, and the surface was very rough to the touch.

The tables below give the experimental data obtained for the above solution, showing the effect of change of acid concentration, the effect of SbF_3 concentration, and the alloying from a fluoride solution of

Pb and Sb, effect of temperature on working conditions, and the effect of current density. For each set of data there is a plotted curve succeeding the same.

Influence of the Change of Acid.

Solution	Acid.	Temp.	Amp.	Volts.	Character of Deposit
75 gr. SbF_3 470 cc. H_2O	100 gr.	50°	.34	1	Large crystals, surface not entirely covered, very rough to touch, a few very large crystals.
" "	50	50	.34	1.56	Crystals smaller, fairly smooth to touch some fairly large crystals growing out of surface.
" "	25	50	.34	2.3	General crystalline, smooth, compact, smaller crystals.
75 gr. SbF_3 470 cc. H_2O 6 gr. gel.	100	50	.34	1.2	Dark, high polish, seldom that a nodule appears.
" "	25	50	.34	1.9	Smooth, burnished, dark deposit, slightly nodular.
" "	10	50	.34	2.5	Smooth, (fairly) burnished, dark, very small nodules, craters.



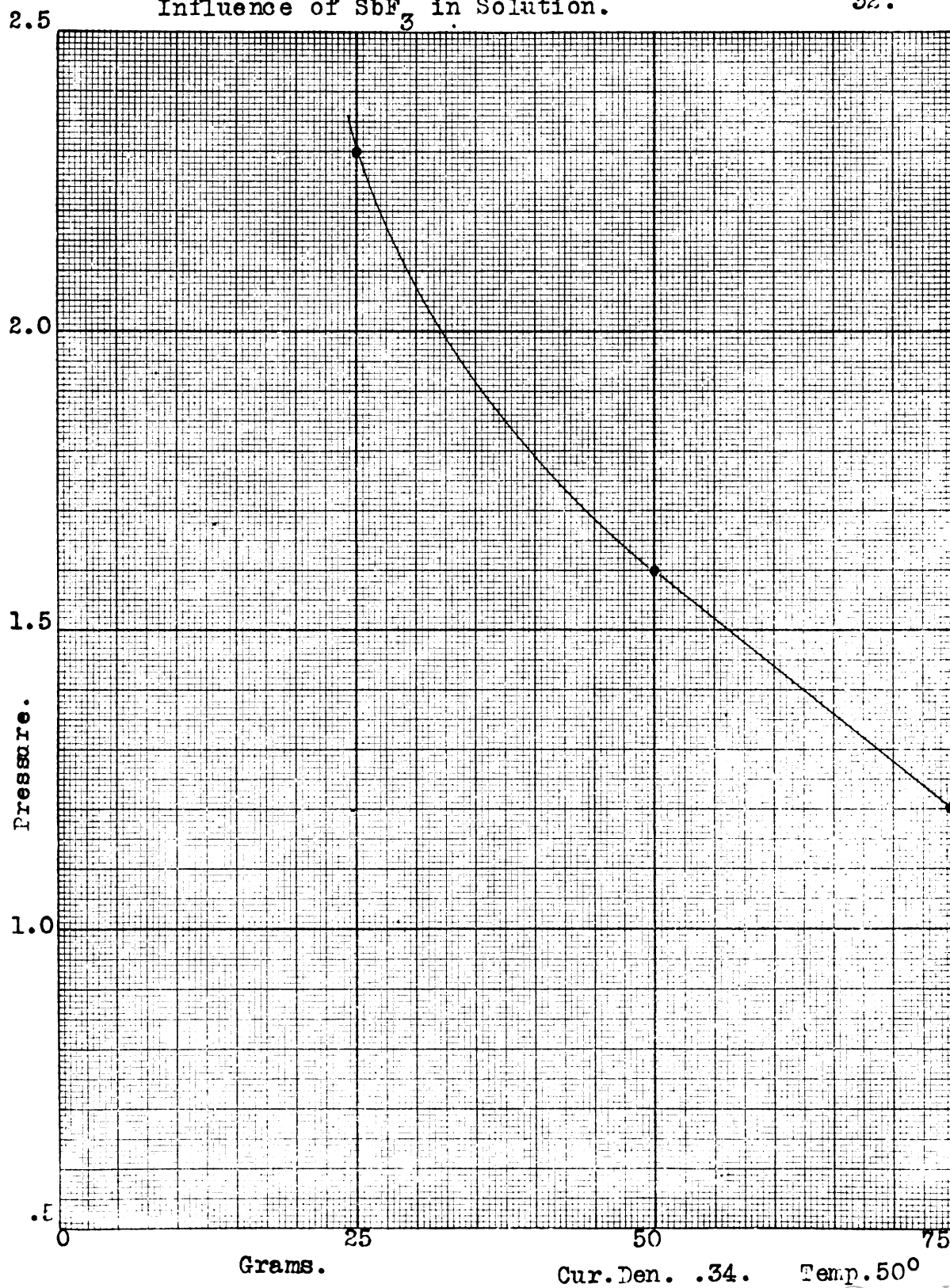
Influence of SbF_3 Concentration.

Solution	SbF_3	Cur.	Den.	Volts	Temp. C	Deposit under Micro- scope.
25 cc. HF 470 cc. H_2O	75 gr.	.34	1.2	50 ⁰		#1. General crystal- line, compact, few (") nodules.
" "	50	.34	1.6	50		#2. Larger crystals than #1, slightly. (")
" "	25	.34	2.3	50		#3 Slightly larger crystals. (")

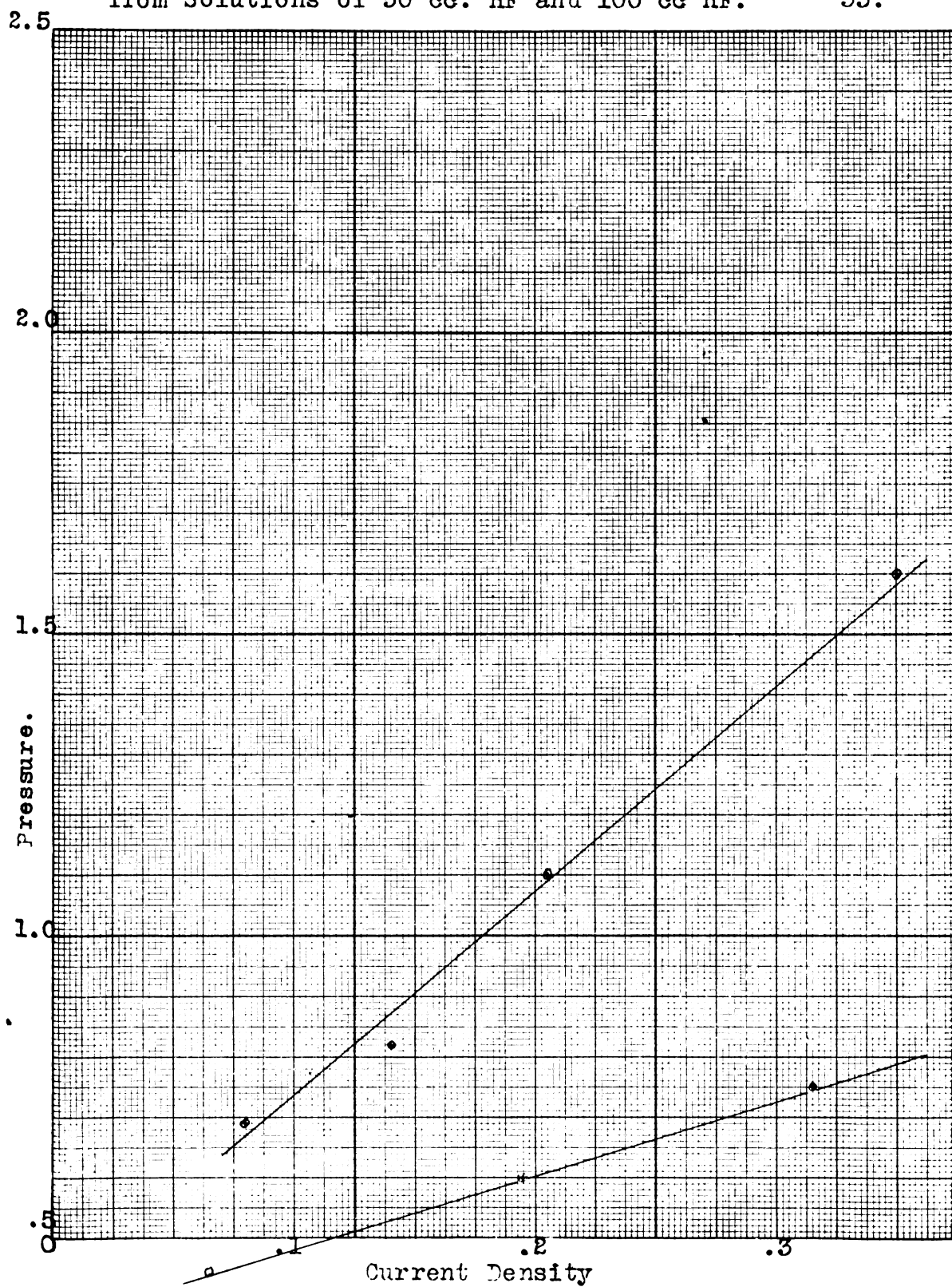
(v) Change of cone has little effect on deposit.

Influence of Gelatine.

Solution	Gel.	Cur.	Den.	Volts	Temp. C.	Deposit under Mi- croscope.
75 gr SbF_3 25 cc. HF 470 cc. H_2O	0	.34	1.2	50 ⁰		General crystalline compact, few nodules.
" "	6 gr.	.34	1.9	50		Fairly smooth, burnished dark deposit, slightly nodular.



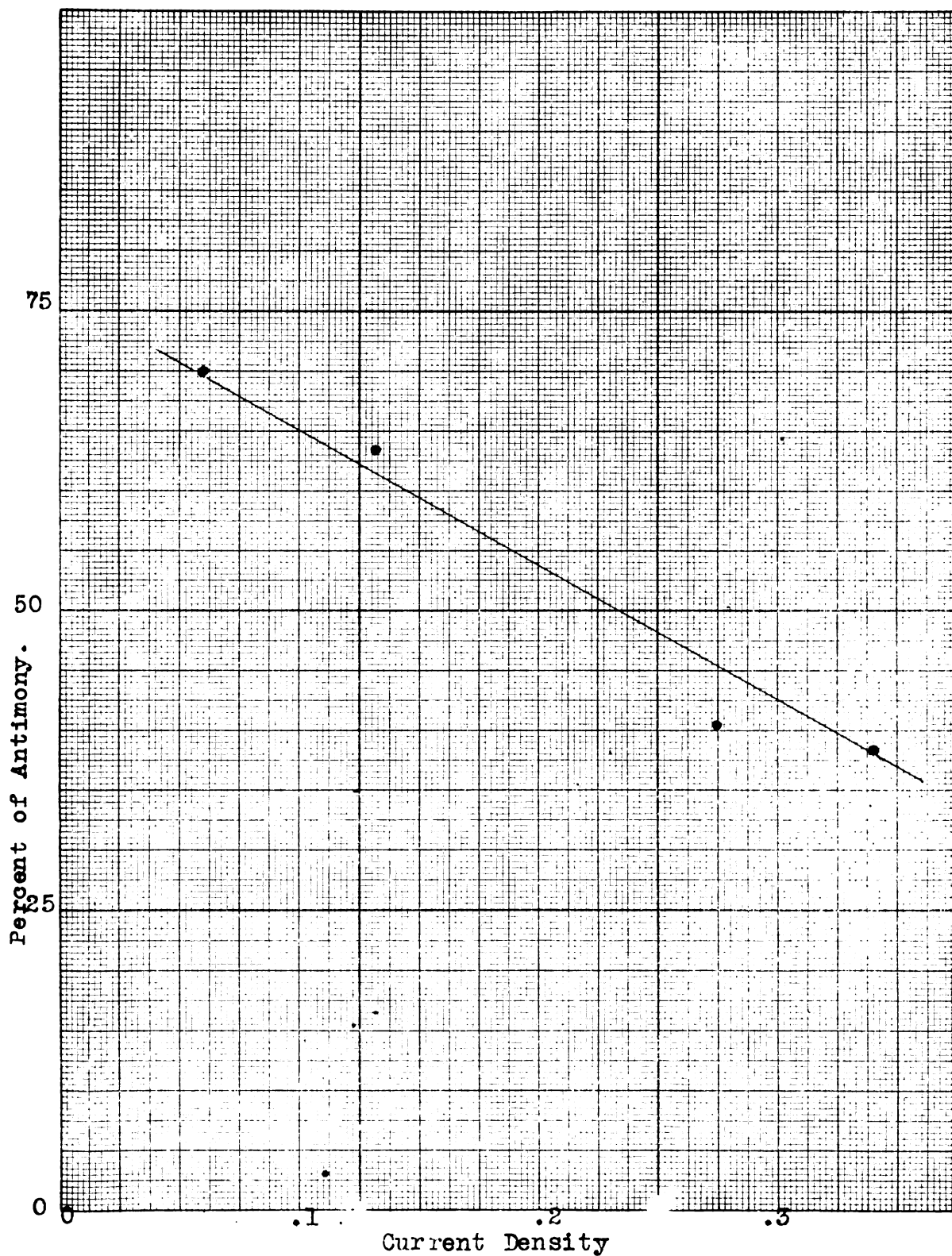
Comparison of Current Density -Voltage Curves
from Solutions of 50 cc. HF and 100 cc HF. 33.



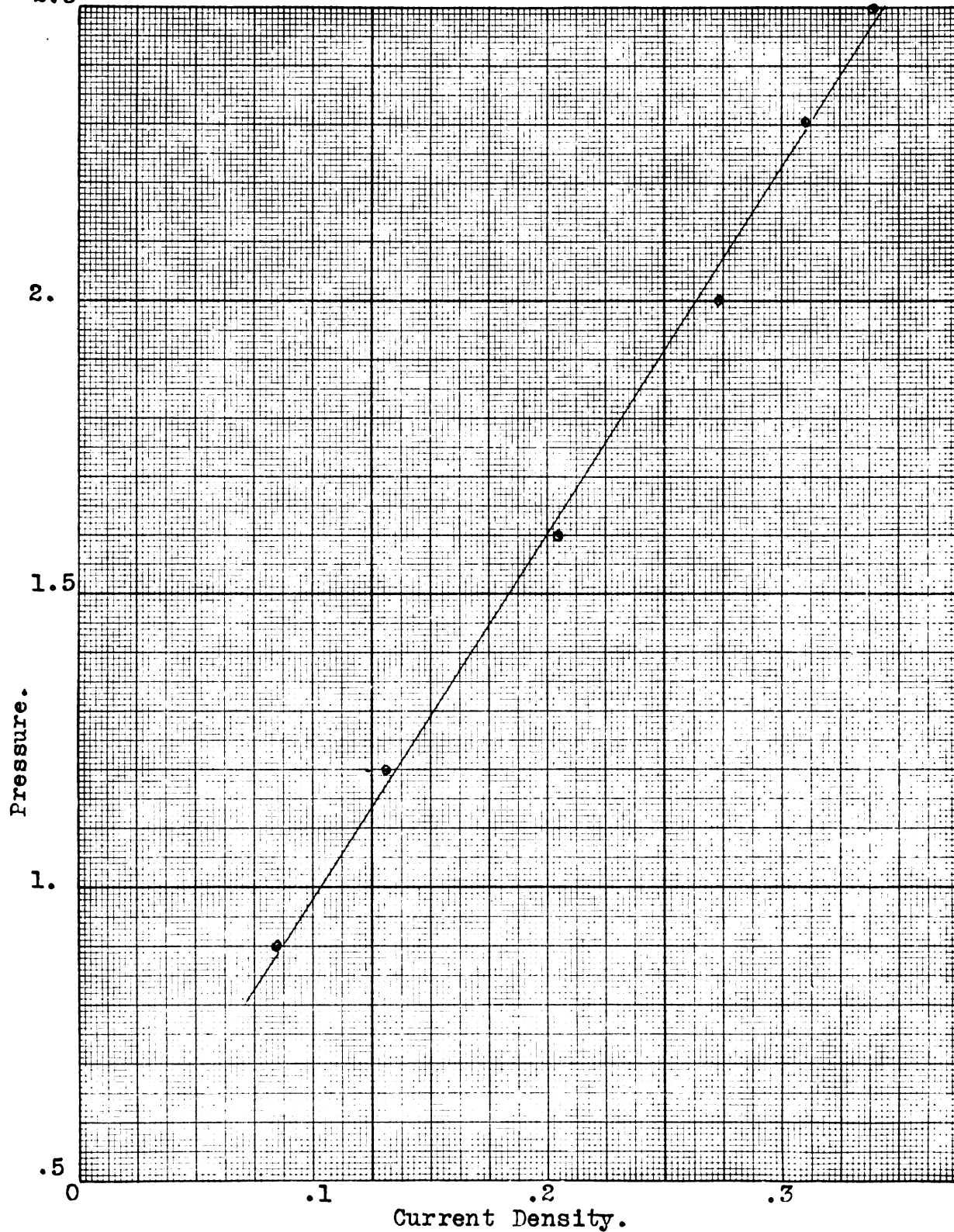
Alloying Pb and Sb from Fluoride Solutions at Different
Current Densities.

Solutions	Gel.	Temp.	Cur.	Volts	Runs	of	Deposits under
	C		Den.		Hrs.	Sb.	Microscope.
75 gr. SbF ₃ 10 cc. HF 470 cc. H ₂ O	6	50°	.0615	--	1	70	
" "	6	"	50	.085	.9	2	Tendency to round crystalline cones.
" "	6	"	50	.132	1.2	1	63.7 Smooth dark sur- face, bright a few grayish spots, a few found nodules
" "	6	"	50	.207	1.6	1	
" "	6	"	50	.273	2.	2	40.4 Grayish, tendency to grow out on edges, surface covered with a jumble of large and small cones.
" "	6	"	50	.307	2.3	1	Very nodular, occasionally one nodule shows tendency to crystalline structure, nod- ules piled up.
" "	6	"	50	.34	2.5	1	38.55

Curves Showing Relation Between 35.
Current Density and Per Cent of Antimony in Alloys..



Current Density - Voltage Curves for Alloying Solution 36.

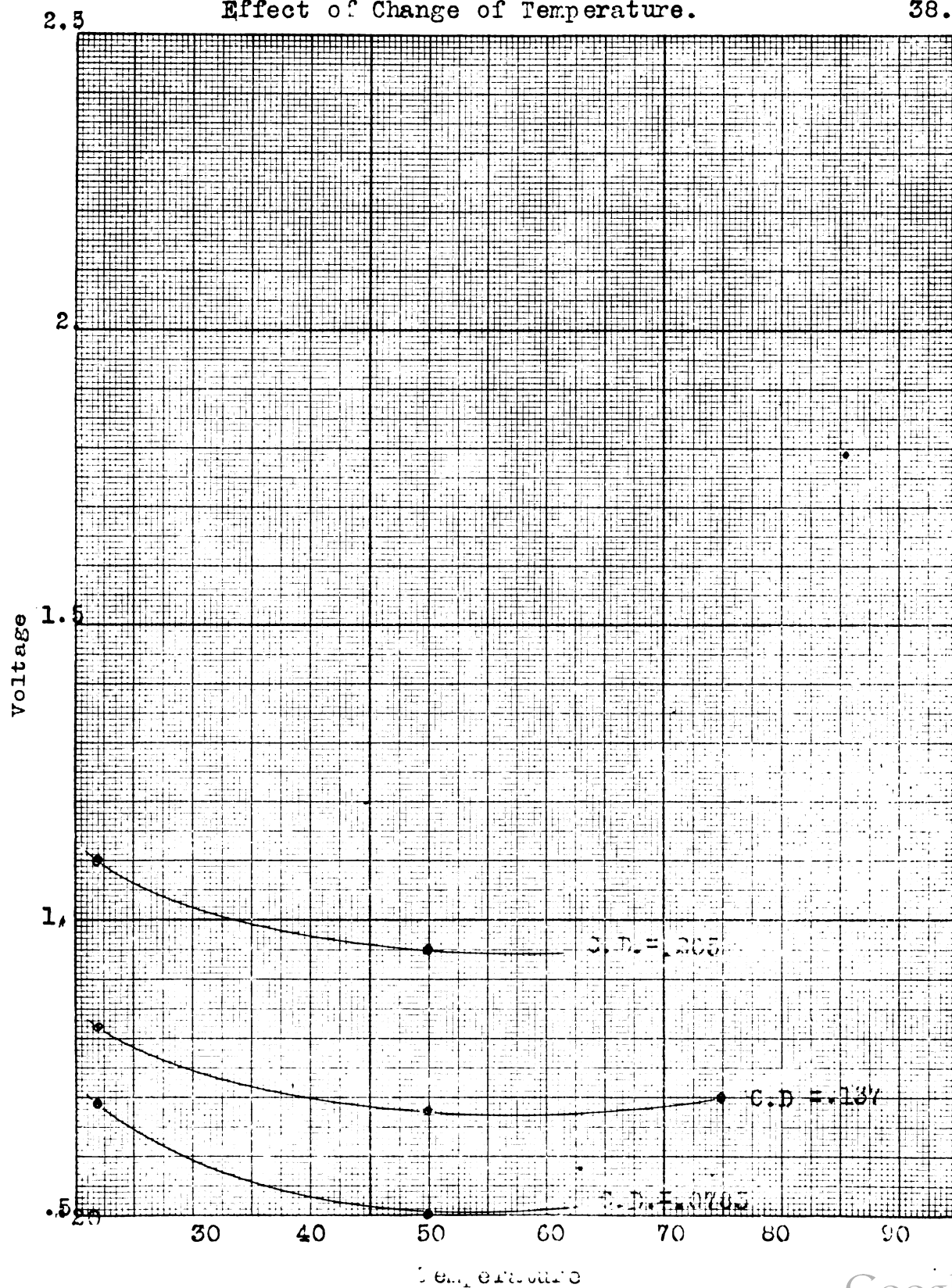


Influence of Change of Temperature.

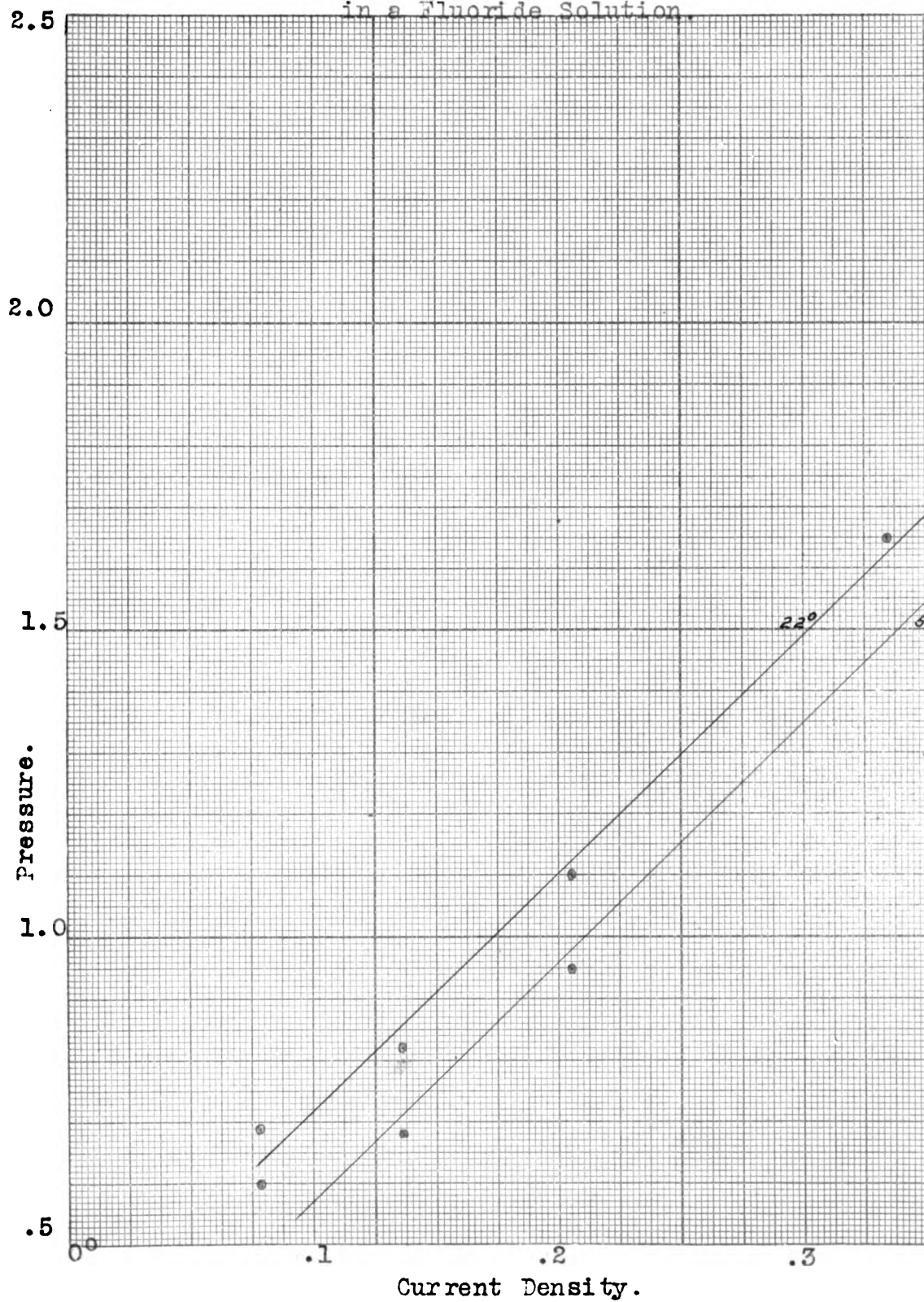
Solution	Temp.	Cur. Den.	Volts	Deposits under Microscope.
75 gr. SbF_3 50 cc. HF 470 cc. H_2O	22	.137	.82	Crystalline, smooth to touch, deposit built of nodules of crystals, deposit quite compact (Cu visible occasionally)
" "	50	.137	.68	Trifle darker deposit, close compact deposit, very even crystalline structure.
" "	75	.137	.7	Deposit still darker, close compact, even crystalline structure. Craters forming in deposit.
" "	22	.0785	.69	Crystalline (small) smooth to touch, nodular in ridges not covering entire plate.
" "	50	.0785	.5	More compact nodular structure, almost entirely gone, leaving a general crystalline deposit.
" "	22	.205	1.1	A trifle rough to touch. Nodular, quite compact, Cu scarcely seen with eye.
" "	50	.205	.95	Background of fine crystals with larger crystals growing out of it.

Effect of Change of Temperature.

38.



Current Density voltage curves at Different Temperat
in a Fluoride Solution.



Current Density Effect.

Solution	Temp.	Cur. Den.	Volts.	Deposits under Microscope
75 gr. SbF_3 50 cc. HF . 470 cc H_2O	22	.0785	.69	Gray deposit. Small crystal- line, smooth to touch, nodu- lar in ridges not covering entire plate.
" "	22	.137	.82	Gray deposit. Crystal more compact, nodular of small crystals. #
" "	22	.205	1.1	Gray deposit. Trifle rough to touch, nodular, quite compact Cu scarcely seen with eye.
" "	22	.335	1.65	Gray deposit. More compact but still of the same char- acter as #.
" "	50	.0785	.5	Darker gray deposit, more compact, nodular structure almost entirely replaced by a general crystalline deposit.
" "	50	.137	.68	Dark gray very even crystal- line structure, compact.
" "	50	.205	.95	Dark gray background of fine crystals increase in ampere hours seems to tend to develop a few large crystals on the surface.
" "	50	.335	--	More large crystals growing out of mass. Deposit be- coming gray again.

Having exhausted the experimentation with the fluoride solution a solution of antimony silico fluoride, similar to the solution used by Betts in depositing lead, was tried. A solution of the composition

150 cc. H_2O

10 cc. H_2SiF_6

was worked with, varying the amount of antimony in the solution from .00218 grams to .109 grams. The antimony was added in cc. of a solution made up and tested to contain .00218 gram per cc. The effect of current density, and gelatine in solution was much more pronounced than with the fluoride bath. As to the current density, even .05 ampere per sq. in. would give a black deposit when only .01 of a gram of antimony was in solution. Seldom could a density of more than .2 be used in any solution without poor results. The voltage in general was much lower for the silico fluoride solution. With gelatine in the solution, even as much as 1. gram, the deposit was not as strong and the best deposit seemed to be from a solution containing about .5 of a gram per 175 cc. solution.

The current density was kept constant as the antimony solution was added. At first the deposit was spongy, black, made up of fine crystals. While the plate

was in the solution the deposit showed a tendency to tree. With the addition of the solution the deposit became grayer until when about 20 cc had been added the deposit was solid, though in ridges, of finely crystalline deposit. The increase beyond this point made the crystals appear smaller. The furrowed appearance still remained.

The effect of change of current density was the most interesting when gelatine was in the solution. Different amounts of gelatine were used, but the best results were obtained when .44 grams of gelatine were added to the solution of 50 cc. Sb solution,

20 cc. H_2SiF_6

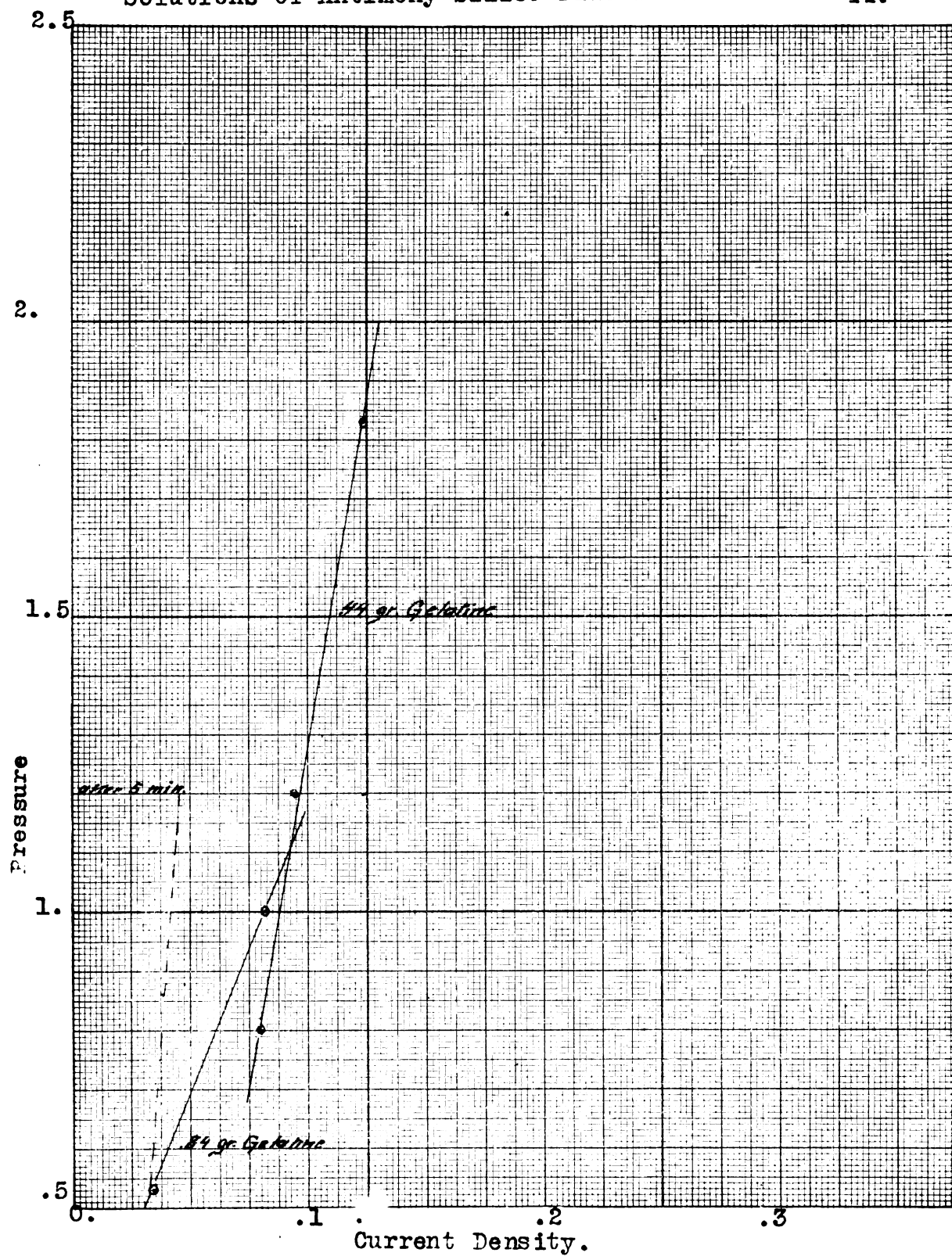
150 cc. H_2O .

A current density was started with .082 ampere per sq. in. at a temperature of 50° - 60° . A little gas was given off at the cathode. With a current density below that given, no gas was noticeable and the deposit was brittle. At this point when the gas comes off, the deposit was silvery white, as bright as a crystalline deposit, yet not crystalline. The electrode would stand bending back and forth up to at least 45° . Beyond this point where the gas was given off more freely the de-
(Vid p.48)

Influence of Change in Current Density in Gelatine
Solutions of SbF and Si Fluoride
Solutions.

Solution.	Gram of Gel.	Cur. Den.	Volts	Temp.	Gas	Character of Deposits
50 cc Sb. solution 20cc. H_2SiF_6 150cc. H_2O	.44	.082	.8	50°	very little gas	Smooth gray deposit, very bright like a crys- talline deposit yet not crystalline, will stand bending, scratches like lead.
" "	.44	.095	1.2	50	gas given off	Smooth. The escap- ing gas divides the surface, scratches into powder.
" "	.44	.123	1.83	50	more gas	Smooth. The escap- ing gas divides the surface scratches into powder.
" "	.64	.082	1.2	50	very little gas	Has lost appearance of rounded crystals although still rough, has become darker. $\frac{1}{7}$
" "	.64	.064	---	50	much gas	Smoothen than $\frac{1}{7}$, still dark.
" "	.84	.034	.53	50		Smooth, tendency to nodular
" "	.84	.082	1.0	50		Gray, very finely crystalline.

Effect of the Change of Current Density in Gelatine
Solutions of Antimony Silico Fluoride. 44.



Change in Current Density.
Antimony Silico Fluoride Solution.

Solution	cc.	Cur.	Temp.	Character of Deposits.
	Sb.	Den.		
sol.				
150cc. H ₂ O				
10cc. H ₂ SiF ₆	8	.0545	60	Very dark, almost black deposit, soft, comes off like fine powder made up of separate crystals.
"	"	.068	60	Surface cut up still, dark soft deposit, crystalline.

Determination of Character of Deposit from Different Solution Concentrations. Antimony Silico Fluoride Solution.

Solution	Sb. Sol. added	Cur. Den.	Temp.	Character of Deposits.
150 cc H ₂ O	2 cc.	.143	60°	
10 cc. H ₂ SiF ₆				
"	" 4 "	.143	60	Dark, smooth, spongy deposit, fine crystals.
"	" 6 "	.143	60	More coarsely crystalline yet still dark, smooth and spongy.

Character of Deposit from Different Solution Concentra-
tions. Antimony Silico Fluoride Solution.

Solution.	Sb. sol.	Cur. Den.	Temp.	Run. Hrs.	Volt- age#	Character of Deposit.
150cc.H ₂ O 10cc.H ₂ SiF ₆	16	.0478	60	1/2		Tendency to dark gray, finely crystalline, compact few nodules (small)
" "	20	.0478	60	1/2		Gray, finely crystal- line deposit, sur- face broken up into valleys running up and down.
" "	26	.0478	60	1/2	.37	The crystals get smal- ler as the Sb solu- tion is added. Smooth deposit still valleys in the deposit. Runs of one hour eliminate this to a great ex- tent.
" "	30	.0478	60	1/2		
" "	34	.0478	60	1/2		
" "	50	.0478	60	1/2		

Very little change in voltage.

Influence of Gelatine in Solution.

Solution	Temp.	Cur. Den.	Volts	Gram Gel.	Character of Deposit.
50cc.Sb Sol. 20cc.H ₂ SiF ₆ 150cc.H ₂ O	50-60	.082	.917	.2	General unevenness like the surface of fine sand or small nodules packed to- gether, smooth tendency to gray.
" "	50-60	.082	.8	.44	Gray smooth, bright like a crystalline de- posit yet not crystal- line, appearance as if crystals were rounded, will stand bending unless at rt. angle.
" "	50-60	.082	1.2	.64	Has lost appearance of rounded crystals, although still rough, has become darker. Be- comes tarnished when plated on Cu. easily.
" "	50-60	.082	1.	.84	Smooth, tendency to nodular, dark deposit. Becomes tarnished when plated on Cu. easily. #

Irregularity in voltage readings due to the fact that with an increase of gelatine the voltage runs up gradually after the switch has been closed. In the one marked # in five minutes the pressure rose to 4 volts. the current dropping proportionally.

posit, although smooth and fairly bright, had a tendency to become darker. This surface when scratched acted like graphite, giving a dust, while in the silvery deposit mentioned above it scratched more like lead.

In making the above more clear, the results were tabulated and plotted below. The tabulations include the influence of gelatine on silico fluoride solutions, the influence of change of current density, and the influence of amount of Sb in solution.

Corrosion tests were tried on antimony from a silico fluoride solution containing an excess of gelatine and antimony from a pure silico fluoride bath. The gelatine deposit was very brittle, easily broken with the fingers, while the other deposit was crystalline and hard. The deposits were shaped on an emery wheel. In a salt solution a test was run for 145 hours. The corrosion for both was about the same, one .0002325, and the other .0001635 gram per square inch per hour. In a 1.2 H_2SO_4 solution run for 268 hours, the corrosion was less marked than in the salt solution, the corrosion here being only .0000123 gram and .0000178 gram.

The corrosion test in 1.2 H_2SO_4 with current was tried. It was found that antimony acted very much like

Al. in this case. A run of 17.5 hours at a current density of .00152 amp. per sq. cm. was made, in which case the deposit from the plain silico fluoride solution lost more than the antimony from the other solution. The total loss anode and cathode were for the gelatine solution .0449 and for the plain solution .1811 gram making a respective loss per hour per square cm. of .000383 gram and .000868 gram respectively.

In further comparison of Sb. and Al. a curve between voltages and currents was plotted for 1.2 H_2SO_4 solution when it was found that the film did not break down until 40 volts were impressed, at which point the current ran up rapidly from .0091 amp. per sq. in. to .0637 to .0728 amp. per sq. in. As a further comparison solutions of phosphoric acid, sodium nitrate, Rochelle salts, sodium phosphate were used in place of the 1.2 specific gravity H_2SO_4 , in which solutions there was always a drop in the current, except in the sodium nitrate solution. A six volt pressure was used for these tests. In the phosphoric acid solution there was a drop of .6 ampere in 2 minutes; in the Rochelle salt solution .2 ampere in one-half minute; in the sodium phosphate .7 ampere in one-half minute.

The data in detail is given below of the action of antimony in different solutions, also of the relative corrodibility of antimony from solutions containing gelatine and pure solutions.

Action of Sb in Different Solutions.

Solution	Temp.	Cur. Den. before	Cur. Den. after	Time in Min.	Volts.
10 gr. phosphoric acid in 50 cc H ₂ O	25°	.0327	.00467	2	6
20 gr. Sodium nitrate in 100 cc H ₂ O	25°	.0532	.0532		6
10 gr. Rochelle salt in 50 cc. H ₂ O	25°	.0373	.028	1/2	9 Remained constant for next 2 min.
10 gr. Sodium phosphate in 50 cc. H ₂ O	25°	.042	.00935	1/2	6

Corrosion Tests.

	Weight plates before	Weight plates after	Loss	Square Cm. area	Hours of Run	Corrosion Gram per hour	Gram per sq. in. per hour.	Sol- ution.
1.	12.5949	12.5651	.0289	31.737	145.75	.000204	.0001635	Conc. NaCl.
2.	2.3529	2.336	.0169	12.675	145.75	.0001159	.0002325	" "
1.	33.9385	33.847	.0915	70.31	268.66		.0000123	1.2 H ₂ SO ₄
2.	13.9125	13.8177	.0948	50.576	268.66		.0000178	" "

1.= deposited, using a current density of one ampere per square decimeter, no gelatine, room temperature.

2.= deposited, using current density of one ampere per 95 square centimeters, excess of gelatine, 50°C.

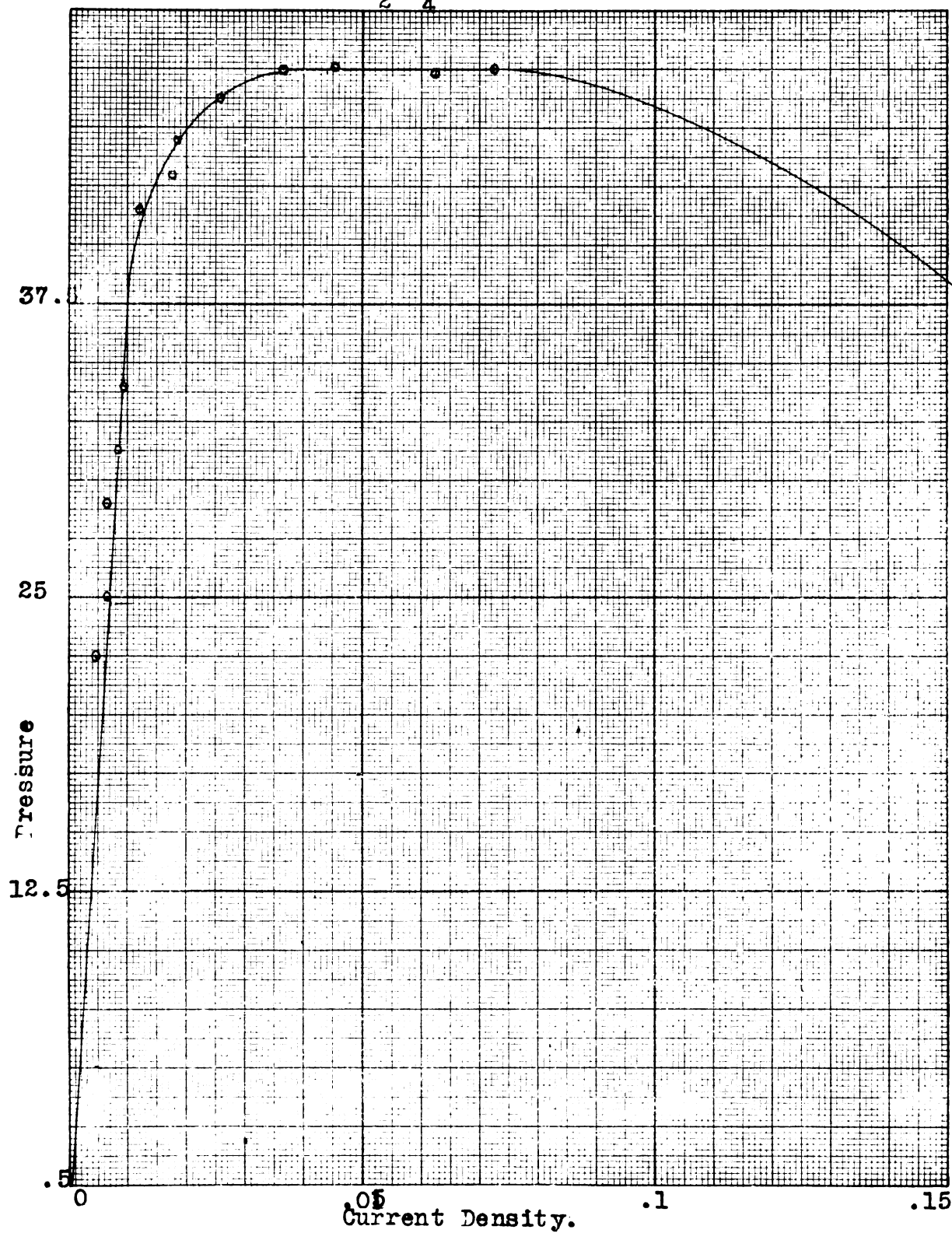
	Wt. plates before	Wt. plates after	Loss in Wt.	Current Density per Sq. In.	Loss in grams per hour per square cen- timeter.
1.Cathode	13.5755	13.5486	.0269	.001524	.00001488
1.Anode	6.0706	5.9164	.1542	.001524	.000853
2. Cathode	2.855	2.8495	.0055	.001518	.000047
2. Anode	2.591	2.5516	.0394	.001518	.000336
----- Solution 1.2 H ₂ SO ₄ . Length of run, 17.5 hours. -----					

Data for Antimony in 1.2 H₂SO₄.

<u>Volts</u>	<u>Amperes</u>
22.5	.0059
25	.00664
29	.00664
31.3	.00864
34	.0091
37	.00955
39	.00955
41.5	.0122
43	.0177
44.5	.0182
46.2	.0259
47.5	.0364
47.6	.0455
47.2	.0627
47.5	.0727
37	.159

Current Density -Voltage Curves for Antimony in
1.2 H₂SO₄.

53.



In conclusion it may be said, after a thorough investigation of references on the subject, that information obtained from such sources was very meager. Besides the above mentioned references, Gore says that a good deposit may be obtained from potassium tartarate of antimony.

Fauntaine recommends a solution of the composition

Sulphate of antimony.....500 grams

Potassium carbonate.....1000 "

Water..... 8 liters.

In referring to this last reference it may be added that owing to the action of antimony in sulphuric acid it was impossible to obtain a deposit of any thickness, for as soon as the current is started, a thin antimony coating appears on the cathode, thus causing the current density to drop off.

This attitude of antimony in H_2SO_4 is hardly applicable for use as a rectifier because the film does not form instantly. In taking the data given above fully one-half minute was allowed for the current to become stationary.

Reference is made by Gore that antimony may be precipitated upon copper and other like electropositive

metals by immersion. This is very true, but the deposit thus obtained is thin and in most cases tarnishes very easily .

None of the solutions used above are of practical importance, generally owing to the brittleness of the deposit obtained from them. The specific resistance of the fluoride solutions was generally higher than that of the silico fluoride. This is generally so marked that such solutions could hardly be used on a commercial scale.

In the case cited, page 43, where a good deposit was obtained, being smooth, bright and gray, ^{it}/withstood bending and scratched much like lead . The objection of using this in practice is that the regulation of current density is necessarily very limited, as shown by a comparison of the data given above; also, that it would be impossible to obtain uniform deposits on uneven surfaces.

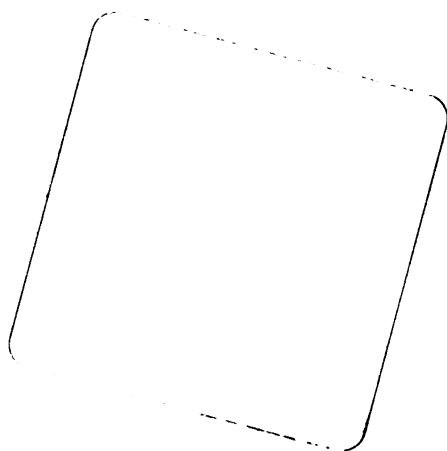
Approved June 4/06 C. F. Burgess.

O. W. Brown.

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